The SOS Nashville 1999 Field Study

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Objectives

- Evaluate the relative importance of the local formation of pollutants versus long range transport for areas with different meteorology and pollutant emission inventories.

- Identify factors that control ozone and fine particle formation in urban and power plant plumes

- Investigate day/night contrasts in chemical and meteorological processes.

ACP Contributions

- Comparison of Ozone Production Rates and Efficiencies in Nashville and Phoenix - Daum et al.
- The Vertical Structure and Downwind Chemistry of the Nashville Urban Plume - Berkowitz et al.
- Airborne Formaldehyde Measurements on the NOAA WP-3 Aircraft - Y-N. Lee et al.
- Ozone Sensitivity to NO_X and VOCs in the Nashville Urban Plume - Kleinman et al.
- Diurnal Variations of Nonmethane Organic Compounds in Downtown Nashville: Impacts on Urban Ozone Production - Doskey et al.

Comparison of Ozone Production Rates and Efficiencies in Nashville and Phoenix - Daum et al.

Conclusions

- The O_3 production efficiencies in Nashville and Phoenix are similar. However, the instantaneous rate is about a factor of two lower in Phoenix than it is in Nashville.

- The difference in O_3 formation rates can be attributed to differences in the primary radical production rate.

- Two thirds of the primary radicals originate from the photolysis of O_3 and the subsequent reaction of $O(^1D)$ with H_2O to form OH.

The Vertical Structure and Downwind Chemistry of the Nashville Urban Plume - Berkowitz et al.

Conclusions

- NO_X loss rates in the Nashville plume were 7%/hour with 4 molecules of ozone produced per molecule of NOx consumed. NO_Z formation rates were 8%/hour.

- During the mid and late afternoon, strong contrasts in the chemistry upwind and downwind of Nashville were found only in the near surface layers of the ABL.

- Significant differences in mixing height around Nashville were attributed to differences in landuse - Forest, agricultural and pasture.

Airborne Formaldehyde Measurements on the NOAA WP-3 Aircraft - Y-N. Lee et al.

Conclusions

- The lowest formaldehyde concentrations were observed over Illinois and Indiana (1.2 ppbv) and the highest over Atlanta, Ga. (5.1 ppbv).
- Within the study region (40-33˚ N latitude) formaldehyde increased from 1.6-5.6 ppbv with decreasing latitude.
- A similar trend was observed for isoprene with levels increasing from 0.16-0.80 ppbv indicating that isoprene is a key precursor of formaldehyde.
- Formaldehyde contributed about 20% of the radical production.
- A strong correlation between formaldehyde and ozone was observed in Atlanta and the Ozark Mountains where isoprene emissions are strong, indicating a role of isoprene in ozone formation.
- Day/night variations of formaldehyde were small suggesting an insignificant nighttime sink.

Ozone Sensitivity to NO_X and VOCs in the Nashville Urban Plume - Kleinman et al.

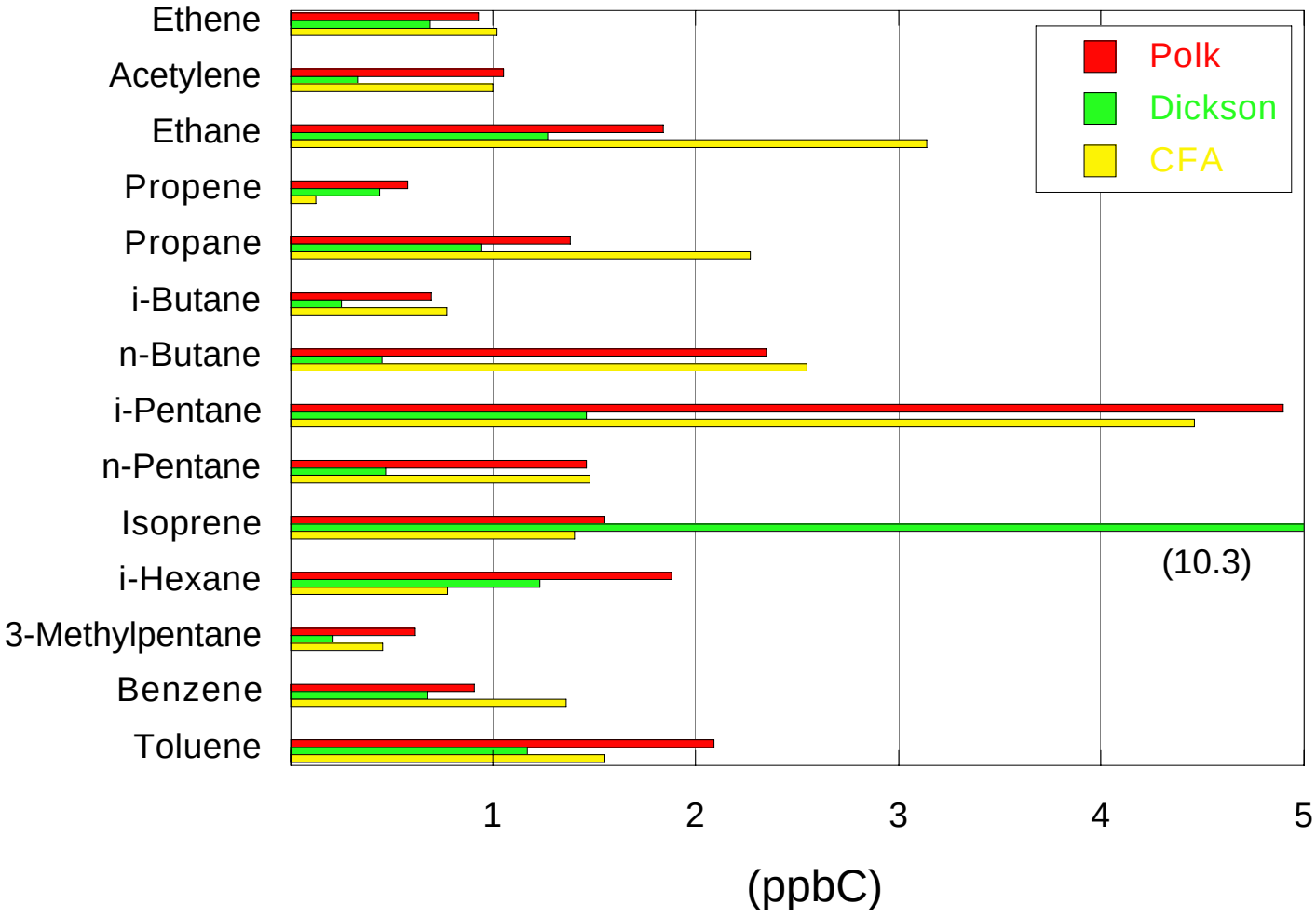
Conclusions

- Diurnal variations of NMOCs in downtown Nashville were similar in 1995 and 1999.

- The ratio of CO/NO_Y decreased from 8.8 in 1995 to 6.3 in 1999.

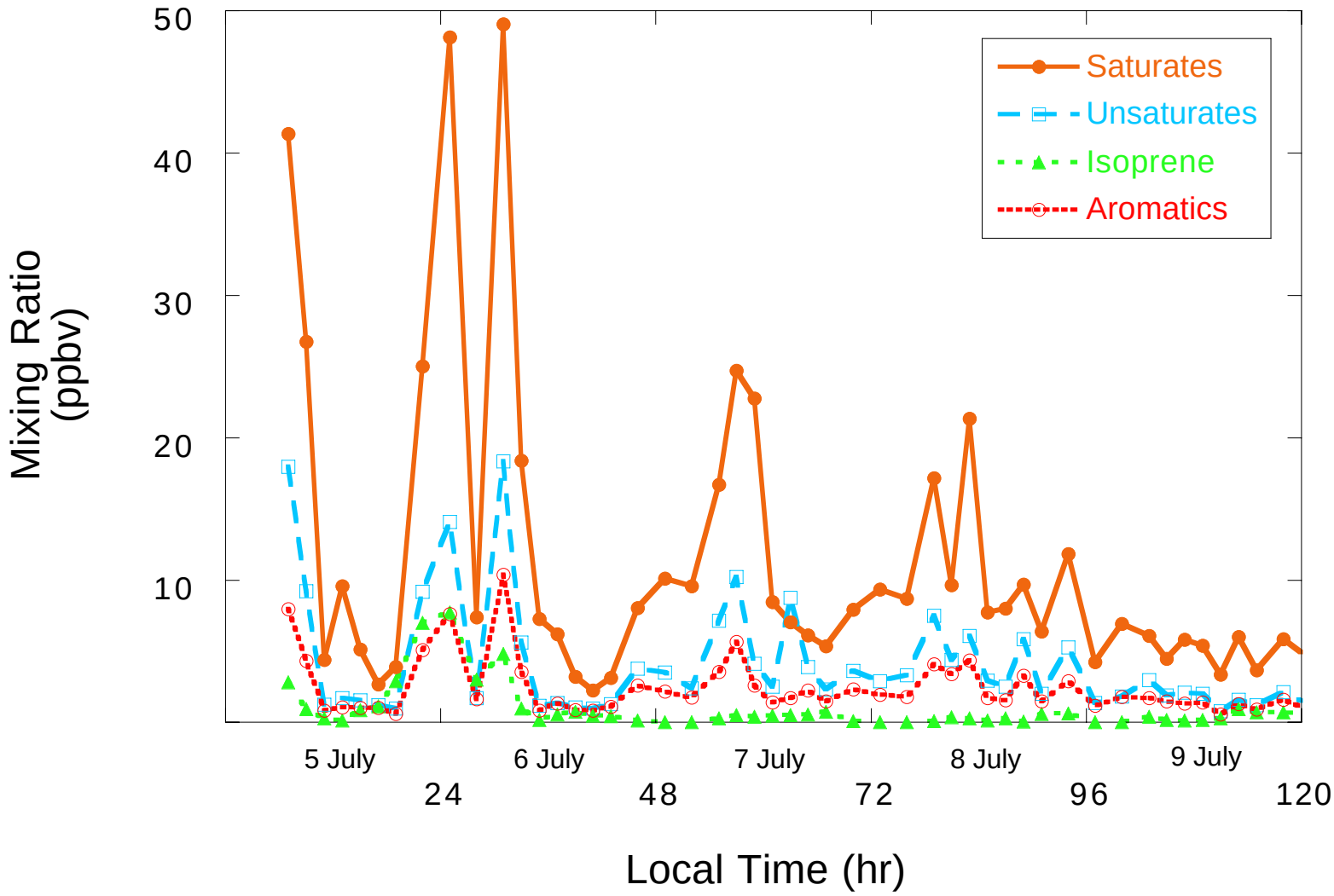
- Levels of NO_X are high in downtown Nashville and O_3 production is limited by the level of NMOCs. A transition to NO_X sensitive chemistry requires an order of magnitude decrease of NO_X in the morning and a factor of 3 decrease of NO_X in the afternoon.

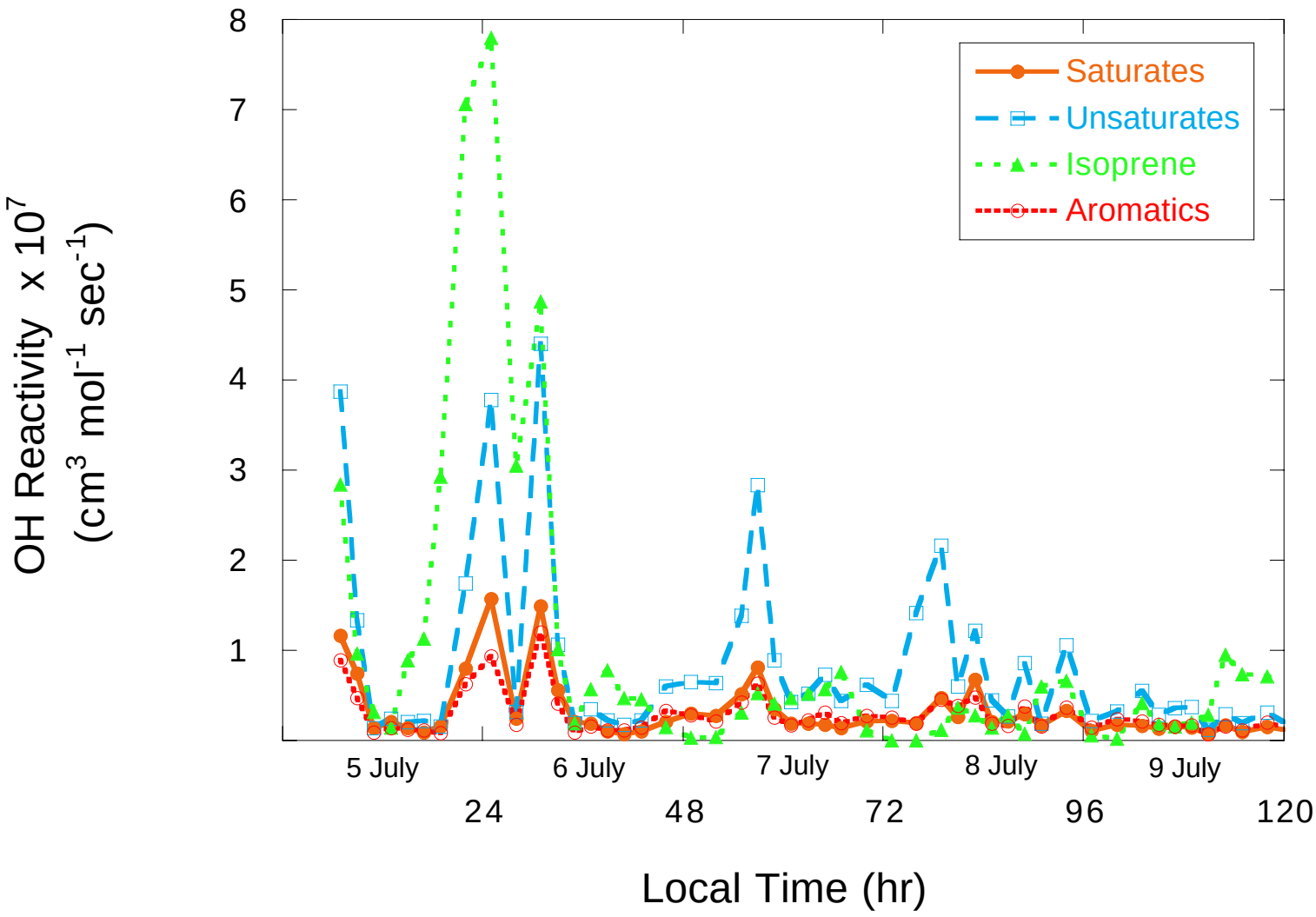
- Approximately 25% of the OH reactivity in the morning and afternoon in downtown Nashville is due to NMOCs of biogenic origin.

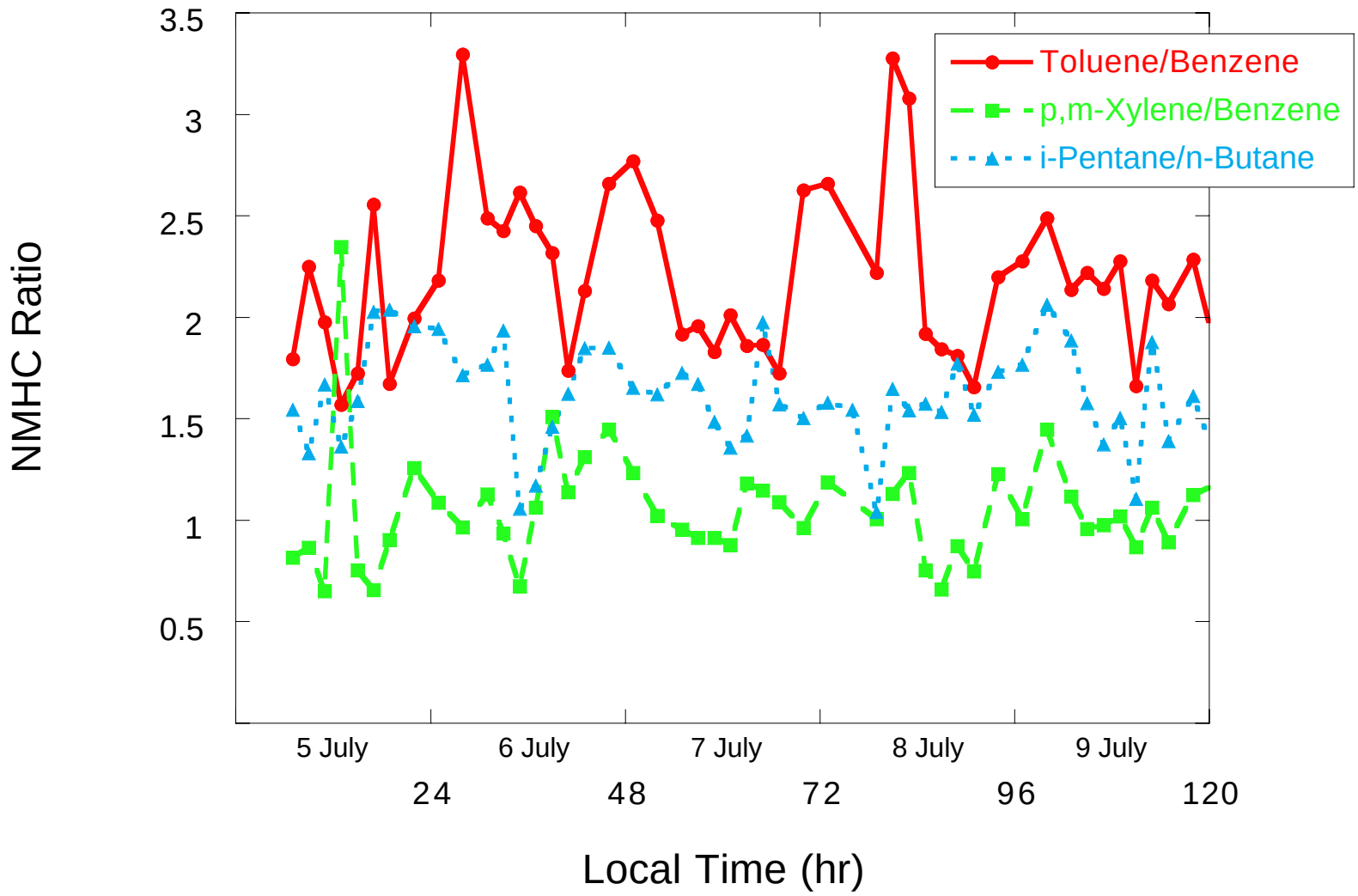

Ethene
Acetylene
Ethane
Propene
Propane
i-Butane
n-Butane
i-Pentane
n-Pentane
Isoprene
i-Hexane
3-Methylpentane
Benzene
Toluene
Polk
Dickson
CFA
(10.3)
1
2
3
4
5
(ppbC)

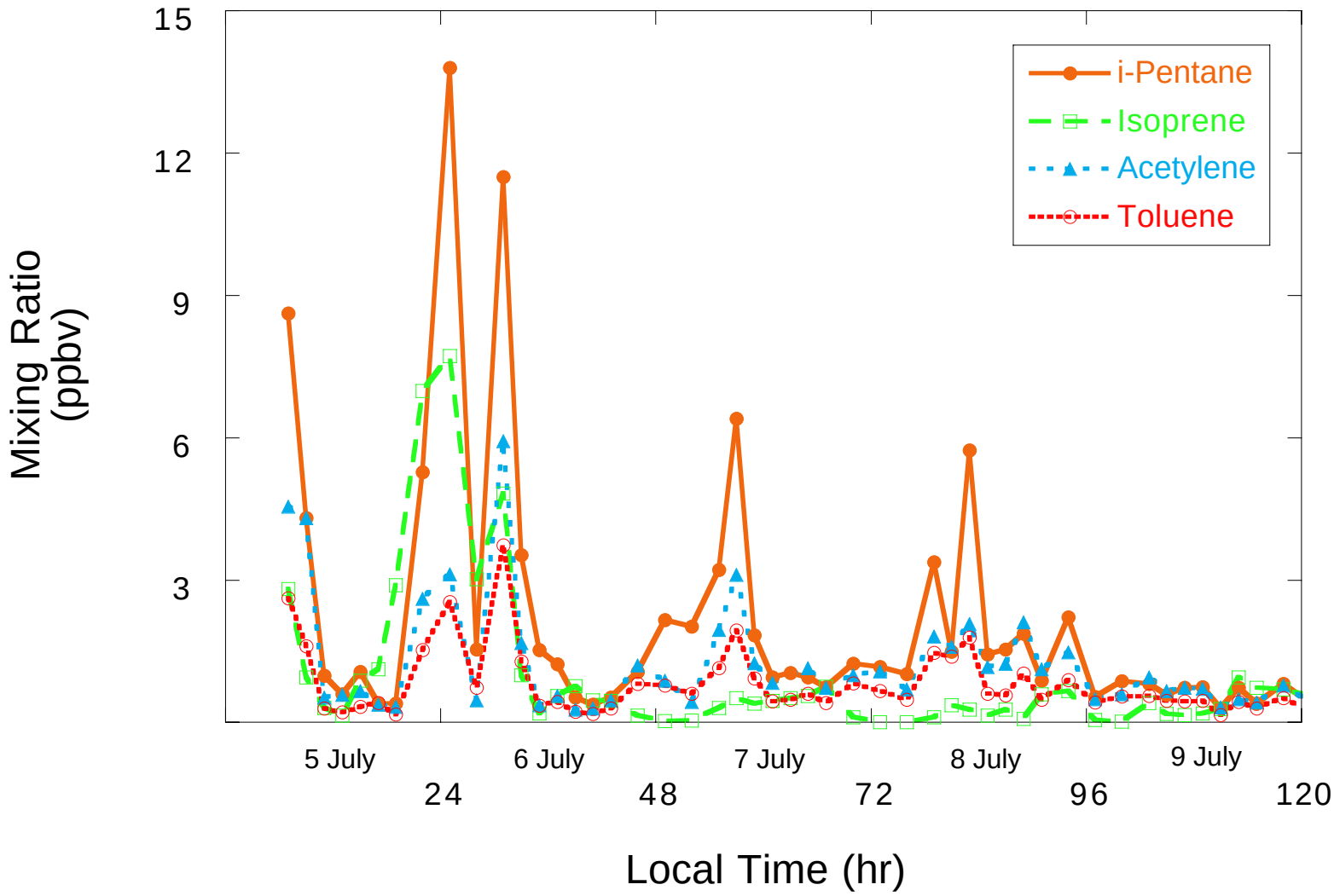
NMOC Measurements in Downtown Nashville

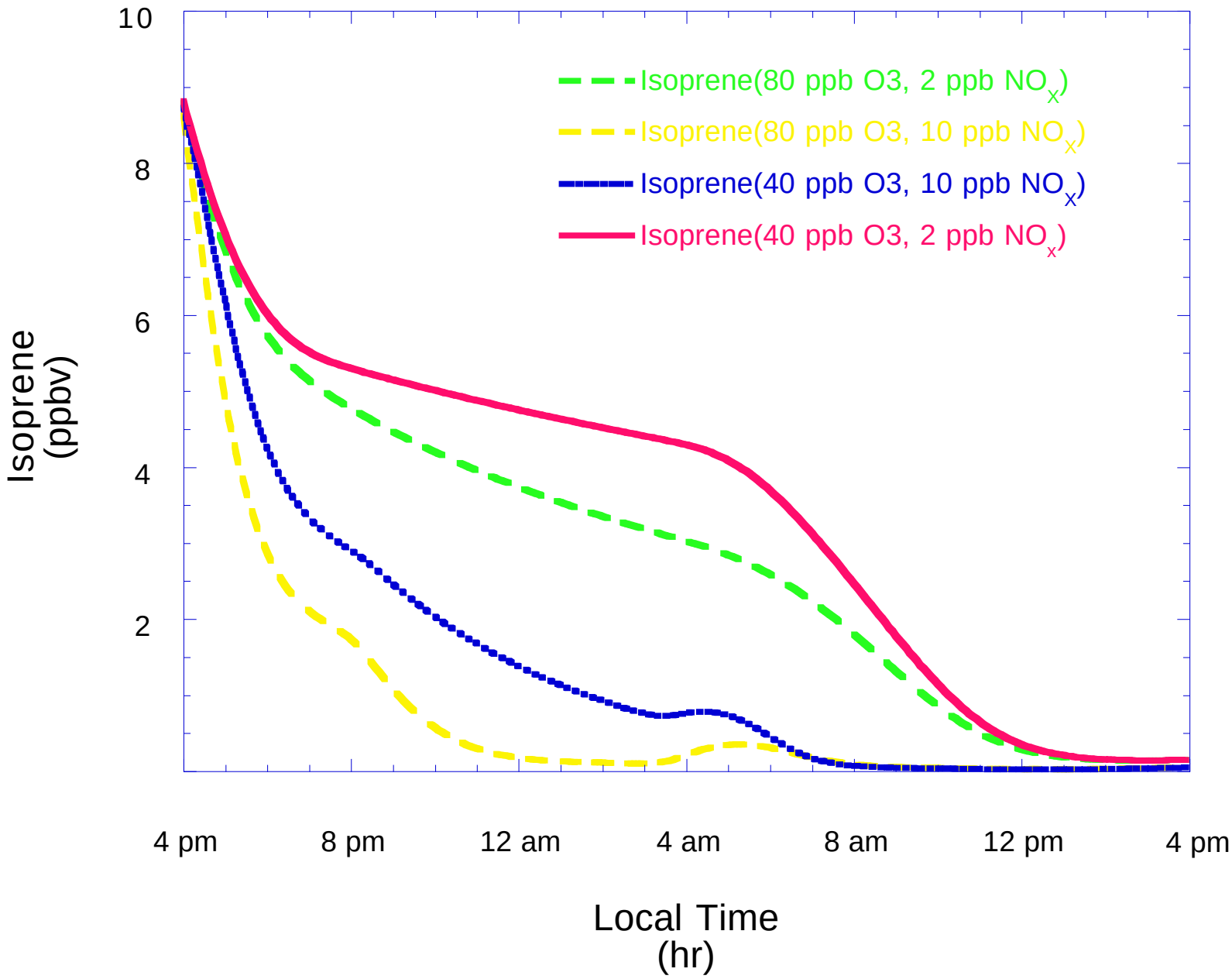
- Site - Polk Building (elevation 100 m).
- Sample collection - Automated 10 canister sampler.
- Sampling Strategy and Frequency - 5 minute sample collected every two hours between 0700 and 1900 LT and every three hours between 1900 and 0700 LT.
- Sample Analysis - In Nashville by cryogenic preconcentration/high-resolution gas chromatography with flame ionization detection.


Saturates
Unsaturates
Isoprene
Aromatics
Mixing Ratio (ppbv)
50
40
30
20
10
5 July
6 July
7 July
8 July
9 July
24
48
72
96
120
Local Time (hr)


OH Reactivity x 10^7
(cm^3 mol^-1 sec^-1)
8
7
6
5
4
3
2
1
Saturates
Unsaturates
Isoprene
Aromatics
5 July
6 July
7 July
8 July
9 July
24
48
72
96
120
Local Time (hr)


NMHC Ratio
3.5
3
2.5
2
1.5
1
0.5
Toluene/Benzene
p,m-Xylene/Benzene
i-Pentane/n-Butane
5 July
6 July
7 July
8 July
9 July
24
48
72
96
120
Local Time (hr)


15
12
9
6
3
Mixing Ratio
(ppbv)
i-Pentane
Isoprene
Acetylene
Toluene
5 July
6 July
7 July
8 July
9 July
24
48
72
96
120
Local Time (hr)


10
8
6
4
2
Isoprene (ppbv)
Isoprene(80 ppb O3, 2 ppb NOx)
Isoprene(80 ppb O3, 10 ppb NOx)
Isoprene(40 ppb O3, 10 ppb NOx)
Isoprene(40 ppb O3, 2 ppb Nox)
4 pm
8 pm
12 am
4 am
8 am
12 pm
4 pm
Local Time (hr)

Conclusions

- Unusually high concentrations of isoprene were measured during the early morning hours of July 6th.
- Back trajectories show the origin of the air to the south, in high isoprene source regions located in Alabama.
- Chemical trajectory modeling calculations suggest that the measured isoprene values are attainable near the Polk Building during the early morning hours if the air-parcel trajectories have low NO_X ($\leq$2 ppb) and moderate ozone (~40 ppb). High ozone (>80 ppb) and high NO_X (~ 10 ppb) in the air parcel will produce less than a few 100 pptv of isoprene.
- High concentrations of NO_y, CO, and NMOCs characteristic of mobile emissions were also measured during the early morning hours of July 6th.
- These observations lead us to conclude that either the isoprene was transported to downtown Nashville and mixed with local mobile emissions or significant emissions of isoprene originate from vehicle exhaust!
- A complete 3-D model calculation using the ANL isoprene emission model and the CMAQ model will be performed to further evaluate this episode.

Biogenic Emissions of Isoprene The Problem

Isoprene emission rates generated by biogenic emission models must be reduced by a factor of 2 for global scale models to accurately predict surface O_3 levels in isoprene source regions.

Previous investigations have verified the isoprene emission algorithm on a scale of 100 km^2 with an uncertainty of about ±25%.

Within the canopy and the lowest layer of the ABL, the time scale of the emission process is less than or equal to the time scale of mixing and chemical oxidation. However, in the middle and upper ABL, chemical oxidation plays a major role in reducing the isoprene concentrations and influencing the vertical fluxes.

Hypothesis

The mass of isoprene that is transported from a forested region to an urban area can be estimated with a three-dimensional chemical transport model that couples an isoprene emission algorithm to the isoprene emission inventory.

The Experiment

Location - Well-characterized deciduous forest

Chemical and meteorological observations

Surface, teathersonde, and aircraft

Vertical profiles of isoprene and its oxidation products

Flux and concentration

Air-Surface Exchange

↑↓

Modeling Studies → Atmospheric Chemistry

↑↓

Transport